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(54) Treatment of cured silicone elastomer

(57) Process for the treatment of a cured silicone elastomer in which at least a part of the surface of the elastomer is contacted with a liquid organosiloxane, preferably a crosslinkable organosiloxane, whereby the elastomer becomes at least partially impregnated therewith. The treatment reduces the absorption of water and/or organic substances by the elastomer and thereby reduces its tendency to discolour, particularly when in contact with the human skin.

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SPECIFICATION

Treatment of cured silicone elastomer

5 This invention relates to a process for the treatment of a cured silicone elastomer to reduce its propensity to absorb liquid substances particularly exudations and components thereof from human skin.

10 Silicone elastomers are now well known commodities which find application in numerous industries. Some applications of silicone elastomers require that they come into contact with aqueous or oily liquids. For example they are increasingly used in the manufacture of prostheses and other articles
15 such as nose pads for spectacles whereby they may be repeatedly in contact with sebum exuded from the skin of the wearer. It has been found that such repeated contact can lead to discolouration of the silicone elastomer. Although the visual effect can be
20 reduced by the incorporation of pigments into the rubber during manufacture this is not always desirable and is not a solution where a translucent or lightly-tinted product is required.

According to this invention there is provided a
25 process for the production of a cured silicone elastomer having a reduced tendency to absorb water and/or organic substances which comprises contacting at least a part of the surface of a cured silicone elastomer with a liquid organosiloxane
30 whereby the cured silicone elastomer becomes at least partially impregnated with the liquid organosiloxane.

The invention further includes an article of cured silicone elastomer whenever obtained by the said
35 process.

Any cured silicone elastomer may be treated according to the process of this invention to reduce its tendency to absorb water or liquid organic substances. Silicone elastomers and methods for their
40 manufacture are well known. Compositions for the production of such elastomers are based on curable organosiloxane polymers, typically those comprising units selected from dimethylsiloxane, phenylmethylsiloxane, diphenylsiloxane, 3,3,3-
45 trifluoropropylsiloxane, methylvinylsiloxane with or without other di- and tri- organosiloxane units, for example trimethylsiloxane, dimethylvinylsiloxane and phenylmethylvinylsiloxane units. The silicone elastomers may be of the heat cured or the so-called
50 room temperature curable types. Thus, for example, the base organopolysiloxane may be converted to a crosslinked (cured) conditions by the incorporation of an organic peroxide or perester and the application of heat, by exposure to high energy radiation or
55 by the addition of silane crosslinking agent with or without a siloxane condensation catalyst. Such elastomers are well known in the art and are described for example in U.K. Patent Specifications Nos. 760451, 764246, 802355, 841825, 862576,
60 957255, 975603, 1272705, 1295194 and 1296302. The silicone elastomer may contain any desired fillers and other additives, for example fume silica, precipitated silica, diatomaceous earth, magnesium oxide and zinc oxide. The process of this invention is

lucent elastomers or those which are only lightly pigmented and where discolouration occurring in use may be unsightly. The preferred silicone elastomers are those which comprise a diorganopolysiloxane containing silicon-bonded vinyl groups, for example in methylvinylsiloxane and/or dimethylvinylsiloxane units, an organohydrogen polysiloxane wherein the silicon-bonded hydrogen atoms may be present in main chain siloxane units and/or
70 terminating siloxane units, and a catalyst for the reaction of silicon-bonded vinyl groups and silicon-bonded hydrogen atoms. Said catalysts are usually platinum compounds or complexes but may be compounds or complexes of other transition metal
75 e.g. rhodium.

The liquid organosiloxane which is employed to contact the silicone elastomer surface preferably has a viscosity at 25°C of less than 200 cS and, more preferably, less than 50 cS. The nature of the
85 substituents attached to silicon in the organosiloxane is not critical and they may include for example, alkyl groups e.g. methyl, ethyl, propyl, pentyl and 2,4,4-trimethylpentyl, alkenyl groups e.g. vinyl and alkyl, aryl groups e.g. phenyl and naphthyl, hydrocarbonoxy groups e.g. methoxy, ethoxy, methoxyethoxy and phenoxy, halogenated alkyl and aryl
90 groups e.g. 3,3,3-trifluoropropyl and chlorophenyl, amino-substituted hydrocarbon groups and mercaptoalkyl groups. Preferably at least 50 percent of the substituents are methyl groups, any remaining substituents being selected from hydrogen atoms, vinyl groups, phenyl groups and alkoxy groups having
95 from 1 to 4 carbon atoms. Examples of the preferred organosiloxanes are polydimethylsiloxanes, poly(methylphenylsiloxanes), poly(methylhydrogensiloxanes), copolymers of dimethylsiloxane units and methylphenylsiloxane units, copolymers of dimethylsiloxane units and methylvinyl siloxane units and poly(methyltrifluoropropylsiloxanes). If
100 desired the organosiloxanes may contain chain terminating units, for example trimethylsiloxane units, dimethylvinylsiloxane units, methylphenylvinylsiloxane units, dimethyl (hydrogen)-siloxane units or methyl dimethoxysiloxane units, or they may
105 be terminated for example with silanol groups.

In general it is believed preferable to convert the liquid organosiloxane, after application to the silicone elastomer, to the crosslinked or gel state. The most preferred liquid organosiloxanes therefore are
115 those which are adapted to such crosslinking by virtue of the presence in the molecule of reactive substituents such as silanol groups, silicon-bonded hydrogen atoms, vinyl groups and alkoxy and other hydrolysable groups. Methods of crosslinking by way of these reactive groups are well known in the art. For example, the liquid organosiloxane may
120 comprise a mixture of an organosiloxane having vinyl groups and an organosiloxane having silicon-bonded hydrogen atoms. Such a mixture of siloxanes can be readily converted to the gel state by the addition of a suitable catalyst, for example chloroplatinic acid or a complex of a platinum compound with an organic or organosilicon compound. A liquid organosiloxane containing silanol groups may be

having at least three reactive groups e.g. acetoxo groups or methoxy groups, and a metal carboxylate catalyst. Alternatively, an organosiloxane having silicon-bonded hydrogen atoms may be employed to cross-link an organosiloxane having silanol groups.

Some impregnation of the silicone elastomer with the liquid organosiloxane may be achieved by merely allowing the elastomer and liquid organosiloxane to remain in contact. Impregnation is more effectively achieved, however, under vacuum, and any suitable vacuum impregnation technique can be employed. A convenient method of operation is to immerse the silicone elastomer (at least partially) in the liquid organosiloxane at or about normal temperature and then to reduce the ambient pressure. The ambient temperature and pressure at which the vacuum impregnation is conducted are not narrowly critical. In general it is preferred to carry out the impregnation procedure at normal or slightly elevated ambient temperatures and at very low pressure, for example 0.001 mm. Hg. The actual temperature and pressure employed in practice will, however, depend on the volatility of the liquid organosiloxane. If the liquid organosiloxane impregnant contains relatively volatile components which it is desired to retain, for example crosslinkers and catalysts, it may be necessary to carry out the impregnation procedure at relatively high pressures e.g. 50 mm. Hg. in order to prevent the loss of these components.

The time for which the liquid organosiloxane and the silicone elastomer are maintained in contact will depend upon a number of factors such as the degree of impregnation required, the nature of the silicone elastomer, the viscosity of the liquid organosiloxane and the ambient pressure. The contact time may therefore vary from less than 5 minutes to more than 10 hours. After removal of the silicone elastomer from contact with the liquid organosiloxane excess organosiloxane may be removed from the surface. When the liquid organosiloxane is crosslinkable the impregnated elastomer may be subjected to any treatment, for example exposure to moist atmosphere or elevated temperatures, required to bring about any desired crosslinking.

The process of this invention may be applied to silicone elastomers of any configuration such as strips, sheets or finished articles of complex shapes. the invention is of particular interest with regard to the treatment of articles of silicone elastomer which are in frequent contact with skin exudations and which are thereby prone to discolouration, particularly nose and ear pieces for spectacle frames. Other examples of such articles are external prostheses and face masks.

The following example in which Me denotes methyl and Ph denotes phenyl illustrates the invention:

Example

A silicone elastomer was prepared by mixing a polydimethylsiloxane having a vinyl group attached to each terminal silicon atom, trimethylsiloxy-terminated poly(methylhydrogen) siloxane and pla-

tinum catalyst. The mixture was cast into sheets of thickness 2 mm. and the sheets cured at 150°C for one hour. The sheets were weighed, and except for one control sample, were each placed in a 500 ml.

glass bottle and covered with one of the following liquids:

- (a) polydimethylsiloxane (viscosity 20 cS at 25°C)
- (b) copolymer of 90 mole % Me_2SiO units and 10 mole % MePhSiO units (viscosity 50 cS at 25°C)
- (c) trimethylsiloxy-terminated poly(methylhydrogen)siloxane (viscosity about 25 cS at 25°C)
- (d) mixture of methylvinylpolysiloxane, methylhydrogenpolysiloxane and Pt catalyst (viscosity about 500 cS at 25°C)
- (e) liquid copolymer of Me_2SiO , PhSiO , PhMeSiO and MeSiO units which is crosslinkable to a flexible siloxane resin.

The bottles were placed in a sealed chamber and the pressure in the chamber reduced to about 30 mm. Hg., the bottles being removed when bubbles ceased to arise from the immersed elastomer, usually after approximately 15 minutes. After pouring off excess liquid the elastomer samples were wiped dry and weighed. All samples except the control exhibited an increase over their pre-treatment weight. The sample treated with (d) was heated to 150°C for 30 minutes to crosslink the impregnant.

The samples were placed in contact with pig fat and examined periodically for discolouration. After 3 months all of the treated samples showed significantly less discolouration than the control.

CLAIMS

1. A process for the production of a cured silicone elastomer having a reduced tendency to absorb water and/or organic substances which comprises contacting at least a part of the surface of a cured silicone elastomer with a liquid organosiloxane whereby the cured silicone elastomer becomes at least partially impregnated with the liquid organosiloxane.
2. A process as claimed in claim 1 wherein the silicone elastomer has been obtained by curing a mixture comprising a diorganopolysiloxane having silicon-bonded vinyl groups, an organohydrogen polysiloxane and a catalyst for the reaction of silicon-bonded vinyl groups and silicon-bonded hydrogen atoms.
3. A process as claimed in claim 1 or claim 2 wherein the cured silicone elastomer is in the form of a nose pad or ear piece for a spectacle frame.
4. A process as claimed in any one of the preceding claims wherein the liquid organosiloxane is convertible to the crosslinked state.
5. A process as claimed in any one of the preceding claims wherein the liquid organosiloxane has a viscosity of less than 50 cS at 25°C.
6. A process as claimed in any one of the preceding claims wherein the cured silicone elastomer is contacted with the liquid organosiloxane under at least a partial vacuum.
7. A process as claimed in claim 1 substantially as described with reference to the Example.

8. A cured silicone elastomer whenever obtained by the process claimed in any one of the preceding claims.

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